Statistical Thermodynamics in Chemistry and Biology

21. The electrostatic potential

Per-Olof Åstrand

D3-119 Realfagsbygget, Department of Chemistry,
Norwegian University of Science and Technology,
per-olof.aastrand@ntnu.no

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Electrostatic potential

This chapter:

- Connection between the electrostatic potential and the electric field.
- Poisson's equation

What is the electrostatic potential?

- Regard the work, δw, required to move a charge, q, a small distance, $d\vec{l}$, in a fixed electrostatic field, $\vec{E}$,

$$\delta w = -\vec{f} \cdot d\vec{l} = -q\vec{E} \cdot d\vec{l}$$

  where the minus sign arises from that the work is carried out against the field and not by the field.
- To move a charge from point A to B,

$$w_{AB} = -q \int_A^B \vec{E} \cdot d\vec{l}$$

- The difference in electrostatic potentials, ψ_B and ψ_A is *defined* as the work, w_{AB} of moving a unit test charge, q_{test}, from point A to point B,

$$\psi_B - \psi_A = \frac{w_{AB}}{q_{\text{test}}} = -\int_A^B \vec{E} \cdot d\vec{l}$$

- The electrostatic potential multiplied by a charge is an energy.

Electric field and electrostatic potential

- To relate the electric field to the electrostatic potential,

$$\Delta\psi = \psi_B - \psi_A = -\int_A^B \vec{E}\cdot d\vec{l} = -\int_{x_A}^{x_B} E_x dx - \int_{y_A}^{y_B} E_y dy - \int_{z_A}^{z_B} E_z dz$$

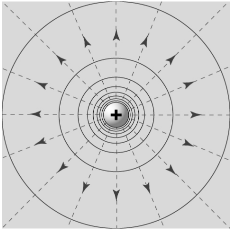
- Now convert from an integral to a differential equation. Assume $A = (x, y, z)$ and $B = (x + \Delta x, y, z)$,

$$\Delta\psi = -\int_x^{x+\Delta x} E_x dx = -E_x \Delta x$$

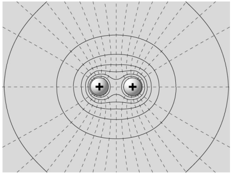
- In the limit $\frac{\Delta\psi}{\Delta x} \to \frac{\partial\psi}{\partial x}$, the electric field is identified as minus the gradient of the electrostatic potential,

$$E_x = -\frac{\partial\psi}{\partial x}\,; \qquad \left(\vec{E} = -\vec{\nabla}\psi\right)$$

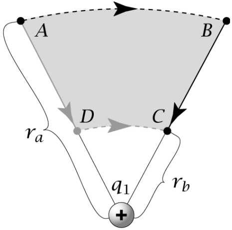
Electrostatic potential surfaces



- Point charge (upper figure)
  - Equipotential surfaces at a constant distances r.
  - The electric field (vectors in the figure) is perpendicular to the equipotential surface.
- Two positive point charges (lower figure)
  - At distances far away, the electrostatic potential behaves as if we have a point charge equal to $2q$.



Electrostatic interactions are conservative forces



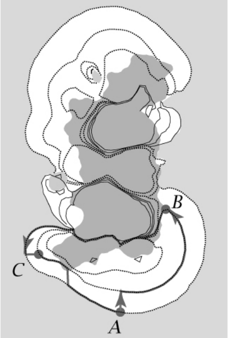
- Electrostatic work is a reversible work and therefore a path-independent quantity that sums to zero around a cycle (upper figure).
- The electric field in spherical polar coordinates,

$$E(r) = \frac{q_1}{4\pi D \varepsilon_0 r^2}$$

- The work of moving a charge q_2 from point A to C,

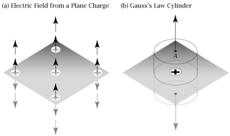
$$w = -q_2 \frac{1}{4\pi D \varepsilon_0} \int_{r_a}^{r_b} \frac{q_1}{r^2} dr = \frac{q_1 q_2}{4\pi D \varepsilon_0} \left(\frac{1}{r_b} - \frac{1}{r_a} \right)$$

- Any path can be approximated by sequence of radial and equipotential segments (example of a protein in the lower figure).



Ex. 20.7: The field from a charged planar surface

- Calculate the field from a charged planar surface (plate of a capacitor, an electrode, or a cell membrane).
- Assuming a “thin” plane, a field both upwards and downwards: the total flux: $2DEA$.
- The surface charge, σ, gives the total charge, σA.
- Gauss’s law gives,



$$2DEA = \frac{A\sigma}{\varepsilon_0} \qquad \Rightarrow \qquad E = \frac{\sigma}{2\varepsilon_0 D}$$

Ex. 21.2: The electrostatic potential in a parallel plate capacitor

- The potential difference, $\Delta\psi$, is given by the work of moving a unit test charge from one side to the other.
- The electric fields E_+ and E_- are given by the previous example,

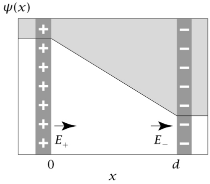
$$E_\pm = \pm\frac{\sigma}{2\varepsilon_0 D}$$

- The force driving a *positive unit charge* has two identical contributions,

$$E_{\text{inside}} = \frac{\sigma}{\varepsilon_0 D}$$

- The potential difference becomes,

$$\Delta\psi = -\int_0^d E_{\text{inside}} dx = \frac{-\sigma d}{\varepsilon_0 D}$$



The electrostatic potential in a parallel plate capacitor

Part 2

- The capacitance, C_0 is defined as,

$$C_0 = \frac{A\sigma}{|\Delta\psi|} = \frac{A\varepsilon_0 D}{d}$$

- What is the electric field outside the plates (answer to Exercise 20.10)?

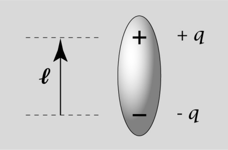
$$E_{\text{outside}} = 0$$

Dipole moment

- The dipole moment, μ, is defined from opposite charges, $\pm q$, separated by a distance, l,

$$\vec{\mu} = q\vec{l}$$

- Leave as exercises:
  - The energy of a dipole moment in an electric field.
  - The interaction between a point charge and a dipole moment.



Poisson's equation

- Using Gauss's theorem (Appendix G, Eq. G.15),

$$\int_{\text{surface}} \vec{v} \cdot d\vec{s} = \int_{\text{volume}} \vec{\nabla} \cdot \vec{v} dV$$

- Substituting $\vec{v} = D\vec{E}$,

$$\int_{\text{surface}} D\vec{E} \cdot d\vec{s} = \int_{\text{volume}} D\vec{\nabla} \cdot \vec{E} dV$$

  relates the *flux* of the electrostatic field *through a closed surface* with the *divergence* of the field *throughout its volume*.
- Substituting Gauss's law (Eq. 20.19),

$$\int_{\text{surface}} D\vec{E} \cdot d\vec{s} = \int_{\text{volume}} \frac{\rho}{\varepsilon_0} dV$$

  gives a the differential form of Gauss's law,

$$D\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0}$$

Poisson's equation
Part 2

- Substituting $\vec{E} = -\vec{\nabla}\psi$ gives

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_0 D} \qquad \text{where} \qquad \vec{\nabla}\cdot\vec{E} = -\nabla^2\psi$$

which is Poisson's equation.

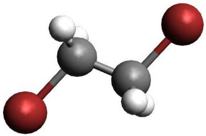
Summary

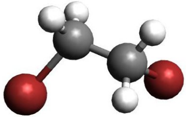
- Discussed the electrostatic potential
- Derived Poisson's equation

Exam August 2011 - Exercise 2

Molecular electrostatics

a) The *trans* and *gauche* conformations of dibromoethane are given in the figure. Dibromoethane has a 3-fold rotation axis around the C-C bond, i.e. a rotation of 120° of one of the -CH_2Br groups moves the molecule from one energy minimum to the next. What is the multiplicity of the *trans* and *gauche* conformation, respectively? Assuming that the energy is the same for all conformation minima, what is the difference in Helmholtz free energy, ΔF, between the *trans* and *gauche* conformation? Which conformation is favoured? The temperature is constant at 300 K.





Exam August 2011 - Exercise 2

Molecular electrostatics - part b)

b) Assume that the energy is determined by the atomic charges of the Br atoms, $q_{Br} = -0.4\ e$. The distance between the two Br atoms is 4.6 Å for the *trans* conformation and 3.7 Å for the *gauche* conformation, respectively. What is ΔF including the Coulomb interaction energy between the two Br atoms in the gas phase (the dielectric constant, $D = 1$)? How does a solvent change ΔF? Is it possible to change the favoured conformation from *trans* to *gauche* (or the other way around) by shifting the solvent?